# EXHIBIT 1

The Research Foundation of State University of New York
University at Albany
Office of Technology Development

# NEW TECHNOLOGY DISCLOSURE

Please submit completed form to Campus Office of Technology Development

1. CAMPUS SUBMITTING THIS DISCLOSURE

   University at Albany

2. TITLE **Molecular Organometallic Resists for EUV (MORE)**

3. KEY WORDS:  Organometallic, Molecular Resist, Cluster, EUV, Lithography

4. TYPE

**X** Invention     ☐ Software     ☐ Video     ☐ Other_____

5. PRIMARY CONTACT (*among developers/inventors*)
Robert Brainard   rbrainard@uamail.albany.edu

6. DATE OF CONCEPTION
June 28, 2011

7. SPONSORSHIP

   ☐ United States Government     ☐ Private Industry     ☐ SUNY     ☐ RF of SUNY     ☐ Personal

   ☐ Other _____

| Name of Sponsor(s) | Research Foundation or Campus Account Number | Sponsored Assigned Identification Number |
|---|---|---|
|  |  |  |

8. PUBLIC DISCLOSURE

   a. Has the description of the technology been published?     ☐ Yes   **X** No   Date:   /  /

   Has the description of the technology been submitted
   for publication?     ☐ Yes   **X** No   Date:   /  /

   Title of Publication_____

   Title of Journal/Other (*specify*)_____

   b. Has the technology been presented at a conference
   or professional Meeting?     ☐ Yes   **X** No   Date:   /  /

C.   Technology *was* not presented.

9.  BRIEF TECHNICAL CONFIDENTIAL DESCRIPTION (*including its unique features*) *ATTACH ANY MANUSCRIPTS, REVIEWS, PAPERS, DIAGRAMS, CHARTS, ETC.*

Since the 1960's, resist manufacturers have been able to meet the needs of the electronics industry (driven by Moore's law), by creating resists based on organic polymers.  Recent indications however, predict that the basic resist design that has been hugely successful in DUV, 193 nm, and early EUV lithography—chemically amplified resists based on organic polymers—may be unable to meet the demands of the 16 and 10 nm nodes because of resolution limits based on acid diffusion lengths, modest etch selectivity, and LER problems in ultra-thin films.  Hafnium oxide nanoparticle resists have recently broke the mold of these conventional organic resists and have shown imaging down to 14-16 nm.[1]

Although these new hafnium oxide resists have shown very good imaging, they have several drawbacks such as instability, poor photospeed (~30-60 mJ/cm2) and requiring extremely concentrated tetramethylammonium hydroxide developer (~2 M).  We propose a new system of EUV resist based on organometallic and inorganic molecules which we have labeled Molecular Organometallic Resists for EUV (MORE).  MORE is a revolutionary new resist technology which would capitalize on the strengths of $HfO_2$ nanoparticle resists, and avoid their weaknesses.  MORE is a system of organometallic or inorganic materials that will have high stopping power for EUV photons and secondary electrons, giving a great deal of control over:

- Particle Size
- Photoreactivity
- Solution Stability
- Particle Defects
- Tunable Properties

Starting with the full periodic table, we have calculated the EUV optical density of the elements from hydrogen ($Z = 1$) to Radium ($Z = 88$) using the standard-state densities with Henke's filter transmission calculator (Table 1).[2]  We found that 38 elements have EUV ODs of $> 11$ /$\mu$m, but from among these, we eliminated those elements that are exorbitantly expensive, radioactive, or toxic leaving a total of 25 elements.  From these 25 elements, a review of chemistry and reactivity led us to 5 classes of compounds.

**The invention is to use thin films of organometallic compounds with high EUV OD and high mass densities (as outlined in Table 1 and shown as examples in the set of five classes of compounds shown below) as high resolution, low LER EUV photoresists.**

- **Mono-Nuclear Organometallic or Inorganic Compounds**
- **Transition Metal Oxide/Oxo-Carboxylate Clusters**
- **Tin Oxoclusters**
- **Bismuth-Clusters**
- **Iron-Sulfide Clusters**

| Z | Symbol | Density g/cm3 | EUV OD/um | Z | Symbol | Density g/cm3 | EUV OD/um | Note | Z | Symbol | Density g/cm3 | EUV OD/um | Note |
|---|--------|---------------|-----------|---|--------|---------------|-----------|------|---|--------|---------------|-----------|------|
| 1 | H | 0.09 | 0.1 | 31 | Ga | 6.1 | 15.9 | | 61 | Pm | 7.3 | 5.5 | |
| 2 | He | 0.1785 | 0.6 | 32 | Ge | 5.35 | 13.1 | | 62 | Sm | 7.52 | 6.9 | |
| 3 | Li | 0.534 | 4.3 | 33 | As | 5.73 | 11.0 | | 63 | Eu | 5.24 | 5.0 | |
| 4 | Be | 1.85 | 0.7 | 34 | Se | 4.81 | 6.5 | | 64 | Gd | 7.9 | 6.8 | |
| 5 | B | 2.31 | 1.6 | 35 | Br | 3.12 | 2.4 | | 65 | Tb | 8.23 | 8.9 | |
| 6 | C | 2.25 | 2.8 | 36 | Kr | 3.74 | 7.7 | | 66 | Dy | 8.55 | 10.9 | |
| 7 | N | 1.25 | 2.8 | 37 | Rb | 1.63 | 0.3 | | 67 | Ho | 8.8 | 10.3 | |
| 8 | O | 1.43 | 4.9 | 38 | Sr | 2.54 | 0.5 | | 68 | Er | 9.07 | 10.9 | |
| 9 | F | 1.69 | 7.5 | 39 | Y | 4.47 | 0.9 | | 69 | Tm | 9.32 | 11.4 | |
| 10 | Ne | 0.9 | 5.3 | 40 | Zr | 6.51 | 1.5 | | 70 | Yb | 6.9 | 8.9 | |
| 11 | Na | 0.97 | 6.3 | 41 | Nb | 8.57 | 2.1 | | 71 | Lu | 9.84 | 10.9 | |
| 12 | Mg | 1.74 | 11.2 | 42 | Mo | 10.22 | 2.6 | | 72 | Hf | 13.31 | 14.0 | |
| 13 | Al | 2.7 | 12.0 | 43 | Tc | 11.5 | 4.9 | | 73 | Ta | 16.65 | 16.5 | |
| 14 | Si | 2.33 | 0.7 | 44 | Ru | 12.37 | 6.9 | | 74 | W | 19.35 | 13.4 | |
| 15 | P | 1.82 | 0.8 | 45 | Rh | 12.41 | 12.6 | $$ | 75 | Re | 21.04 | 16.1 | $$ |
| 16 | S | 2.07 | 1.4 | 46 | Pd | 12.02 | 18.8 | $$ | 76 | Os | 22.6 | 17.6 | $$ |
| 17 | Cl | 3.21 | 2.6 | 47 | Ag | 10.5 | 32.1 | | 77 | Ir | 22.4 | 17.9 | $$ |
| 18 | Ar | 1.78 | 1.6 | 48 | Cd | 8.65 | 22.2 | Tox | 78 | Pt | 21.45 | 24.3 | $$ |
| 19 | K | 0.86 | 0.9 | 49 | In | 7.31 | 28.3 | | 79 | Au | 19.32 | 20.9 | $$ |
| 20 | Ca | 1.54 | 1.4 | 50 | Sn | 7.31 | 29.4 | | 80 | Hg | 13.55 | 18.0 | Tox |
| 21 | Sc | 2.99 | 3.7 | 51 | Sb | 6.68 | 27.2 | | 81 | Tl | 11.85 | 17.0 | Tox |
| 22 | Ti | 4.5 | 7.0 | 52 | Te | 6.24 | 30.3 | | 82 | Pb | 11.35 | 19.9 | Tox |
| 23 | V | 5.96 | 9.8 | 53 | I | 4.93 | 23.6 | | 83 | Bi | 9.75 | 22.4 | |
| 24 | Cr | 7.2 | 15.6 | 54 | Xe | 5.9 | 29.8 | | 84 | Po | 9.3 | 22.5 | RA |
| 25 | Mn | 7.47 | 13.0 | 55 | Cs | 1.87 | 7.9 | | 85 | At | | | RA |
| 26 | Fe | 7.86 | 21.0 | 56 | Ba | 3.59 | 2.9 | | 86 | Rn | 9.73 | 29.7 | RA |
| 27 | Co | 8.92 | 26.7 | 57 | La | 6.15 | 2.0 | | 87 | Fr | | | RA |
| 28 | Ni | 8.9 | 29.2 | 58 | Ce | 6.77 | 2.5 | | 88 | Ra | 5.5 | 21.0 | RA |
| 29 | Cu | 8.94 | 24.7 | 59 | Pr | 6.77 | 3.0 | | | | | | |
| 30 | Zn | 7.14 | 22.4 | 60 | Nd | 7.01 | 5.2 | | | | | | |

**Table 1. Optical and mass densities of first 88 elements.** Elements marked with $$ have been rejected because they are too expensive; elements marked with RA have been rejected because they are radioactive; elements marked with Tox have been eliminated because they are too toxic.

*For a detailed description of this invention, please see Appendix A.*

1. Impria Presentation; Sematech RMAG, Albany, NY, May 25, 2011.
2. http://henke.lbl.gov/optical_constants/filter2.html

10. PROTOTYPES AND/OR SAMPLES

    a. Is a working prototype available for demonstration?    ☐ Yes  X No  ☐ N/A

    b. Are samples (e.g. compounds) available for testing?    ☐ Yes  X No  ☐ N/A

11. ADVANTAGES OF THE TECHNOLOGY (*relative to existing technology*)

1. MORE resists should have tight control over particle size, have long shelf-life, lower etch rates and lower particle defects than conventional resist platforms.

2. MORE resists should have extremely high resolution imaging in EUV.

*For a detailed description of this invention, please see the Appendix A.*

## 12. POSSIBLE DISADVANTAGES OF THE TECHNOLOGY *(relative to existing technology)*

None.

## 13. NON-CONFIDENTIAL DESCRIPTION OF THE TECHNOLOGY
*(indicate applications and advantages -- for marketing purposes)*

This invention concerns the development of a high resolution resist technology for printing 10 nm lines using EUV lithography.

## 14. LIST COMPANIES THAT YOU BELIEVE WOULD BE INTERESTED IN COMMERCIALIZING THE TECHNOLOGY

| Company Name | Contact (if any) | Location/Telephone Number |
|---|---|---|
| Intel | Wang, Yueh | |
| Sematech | | |
| | | |

# Appendix A.

# Molecular Organometallic Resists for EUV (MORE)

Robert Brainard, Brian Cardineau, Dan Freedman, Greg Denbeaux

August 1st, 2011

**Executive Summary.** The purpose of this three-year proposal is to invent revolutionary new photoresists based on Molecular Organometallic Resists for EUV (MORE) that will be capable of meeting the needs of the 10-nm node. The proposed work will be to initially screen a broad selection of materials with the capability of stopping EUV photons in 20 nm films (high EUV OD), and converting them into secondary electrons with short diffusion lengths causing a photochemical change that will result in negative or positive tone imaging. We propose that this approach is the best way to meet the LER and sensitivity needs of EUV resists capable of resolution down to 10-nm half-pitch.

**This innovative technical approach will share some of the advantages of the Inpria HfO$_2$ Nanoparticle approach:**

- High EUV OD (better photon statistics),
- High stopping power of secondary electrons (less electron blur),
- Excellent etch resistance,

**Yet will open the door to an overall better solution because of:**
- Smaller size (molecular *vs.* particles),

- Better shelf-life (solutions *vs.* particle suspensions),
- Better sensitivity (better control of thermodynamics and kinetics of photochemical reactions),
- Fewer defects (molecular *vs.* particles),
- Better IP position for Intel (only SUNY and Intel involved).

During Year 1, we will screen 22-46 inorganic or organometallic materials for use as EUV resists and down-select to 3-5 resist platforms. In Year 2, we will optimize the synthesis, composition, formulation, and processing of these new resist platforms to reach 10-nm resolution. In Year 3, we will further refine the performance of our best lithographic systems by combining photochemical mechanistic studies with compositional advances to improve the LWR and sensitivity of these resists. Ultimately, we will work with Intel to seek-out one or more commercial suppliers of the successful 10-nm resist technologies. Over the course of the program, CNSE will primarily use the BMET and AMET shifts it receives from Sematech, but will request 2-4 shifts/year from Intel (see Budget). The cost of the program will be $224.5K/year for three years.

## 1. Introduction and Proposal Overview

### A. Background Leading to Proposed Research

Since the 1960's, resist manufacturers have been able to meet the needs of the electronics industry (driven by Moore's law), by creating resists based on organic polymers. This has been true, as well, for resists designed for EUV (13.5 nm) lithography up to about 22 nm. However, recent indications are that the basic resist design that has been hugely successful in DUV, 193 nm, and early EUV lithography—chemically amplified resists based on organic polymers—may be unable to meet the demands of the 16 and 10 nm nodes because of resolution limits based on acid diffusion lengths, modest etch selectivity, and LER problems in ultra-thin films.

Fortunately, one disruptive technology, based on hafnium oxide nanoparticles, has shown a new pathway for EUV resist design. Two groups are currently pursuing different variations of this technology: *Inpria* which uses $HfO_2$ nanoparticles suspended in water and Cornell which uses suspensions of $HfO_2$ nanoparticles suspended in water or organic solvents. Our group is currently collaborating with the Cornell research group. Figure 1 compares these two nanoparticle-based technologies.

### Impria Characteristics
- Best EUV resolution in the world (14-16 nm)
- Anionic suspension in water
- Poor photospeed (~30-60 mJ/cm$^2$)
- Requires high normality TMAH (~2 M)
- Negative tone imaging based on reductive elimination of $O_2$ to form peroxide linkages.

### Cornell $HfO_2$ Nanoparticles
- Surfactant-based nanoparticles suspended in water or organic solvents.
- Free radical negative-tone imaging.
- Demonstrated 25 nm isolated lines with 6.6 mJ/cm$^2$ dose.
- Excellent etch resistance. Etch selectivity 4 times greater than PHS.

**Figure 1.** Comparison of Inpria and Cornell $HfO_2$ Imaging Systems.

### B. Why do $HfO_2$ Resists Perform so well in EUVL?

In our opinion, there are three reasons:

**(1) EUV OD.** $HfO_2$ is significantly darker (higher optical density, lower transmittance) than organic polymers. Given the high energy of EUV photons, and consequently, the low number of photons/mJ of light, it is important to absorb as many photons as possible to minimize the LWR caused by shot-noise. This noise is inversely proportional to $\sqrt{N}$, where N is the number of absorbed photons.[1-3] In his plenary talk at SPIE this year, Jim Thackeray[4] said that his target transmission for EUV resists is 50%. To print 10-nm lines with an aspect ratio of 2:1, film thickness must be around 20 nm. Polyhydroxystyrene at this thickness will stop only ~10% of the light (T $\cong$ 0.90)(Figure 2). Loading up organic polymers with fluorine will have only limited impact. Teflon (($C_2F_4)_n$) probably contains the most fluorine possible in an organic polymer, yet it only stops ~30% of the light in a film of 20 nm (T $\cong$ 0.70). A continuous, 20 nm film of $HfO_2$, on

the other hand, will stop ~50% of the EUV light. Although accounting for the 24% void space in closest packed spheres, and 30% of mass taken up by surfactant, the EUV transmittance of a $HfO_2$ resist is probably closer to 64%.

|  | Literature Densities | Calculated Densities |
|---|---|---|
| $HfO_2$ Dense Film | $\rho$ = 9.7 g/cm3<br>T = 0.53 | $\rho$ = 11.5 g/cm3<br>T = 0.47 |
| $HfO_2$ NanoPart. With 30% Ligands |  | $\rho$ = 6.5 g/cm3<br>T = 0.64 |
| PTFE | $\rho$ = 2.2 g/cm3<br>T = 0.69 | $\rho$ = 1.8 g/cm3<br>T = 0.74 |
| PHS | $\rho$ = 1.2 g/cm3<br>T = 0.92 | $\rho$ = 2.0 g/cm3<br>T = 0.87 |

**Figure 2.** Comparison of EUV Optical Density (OD) and Mass Density of three representative materials. We compare our ability to model mass density with actual experimental values. The model for predicting the mass density (g/cm$^3$) of compounds is described in more detail in Section 3B.

**(2) Mass Density.** $HfO_2$ has 5-8X greater mass density than do organic polymers (Figure 2). This greater mass density is a significant factor in determining the extent of electron blur and/or electron diffusion length. In other words, the scattering and secondary electrons produced in a high mass-density material will be significantly more localized than in a lower density material such as an organic polymer, giving additional opportunities for improving resolution due to reduced electron-blur.

**(3) No Acid Diffusion.** The Inpria resist, which shows the best resolution in the world at this time, does not involve an exposure mechanism based on chemical amplification.[5,6] As has been discussed in the literature for some time,[7] acid diffusion in chemically amplified resists can significantly limit the research capability of EUV resists.

Although resists based on $HfO_2$ nanoparticles show excellent resolution and LWR (Inpria) and good promise (Cornell), we think that resists based on $HfO_2$ nanoparticles have fundamental limitations which will prevent them from meeting the needs of EUV resists for the 10-nm half-pitch imaging. We propose that resists composed of molecular organometallic or inorganic compounds with high EUV OD, high mass-density, and without chemical amplification will provide the best pathway for printing 10 nm lines.

**C. This Proposal**

We propose to develop revolutionary new resist technologies which would capitalize on the strengths of $HfO_2$ nanoparticle resists, and avoid their weaknesses. We propose to evaluate a large number of organometallic compounds and eventually produce a resist that will have high stopping power for EUV photons and secondary electrons, yet will have a number of advantages over the $HfO_2$ nanoparticle resists as described below.

**(1) Size.** The nanoparticles in the existing $HfO_2$ resists are 2-3 nm in diameter. It will not be possible to print 10 nm lines with < 1 nm LWR with particles of this size. The organometallic compounds proposed here will be 0.5 to 1 mm in diameter.

**(2) Control over Photoreactivity.** The $HfO_2$ nanoparticles are, quite literally, small pieces of mineral and, as such, are at a thermodynamic minimum. The proposed photochemical reaction of the Inpria resist (reductive elimination of $O_2$)[8] is very much fighting up-hill with regard to thermodynamics, which is no doubt a principle reason that the resists are so slow.

**(3) Dispersions vs. Solutions.** Dispersions of nanoparticles are difficult to stabilize since these suspensions are often prone to gravitational settling and flocculation; whereas solutions of molecules can be stable indefinitely.

**(3) Particle Defects** created by the flocculation of the $HfO_2$ nanoparticles are a serious concern. We propose that resists based on inherently soluble molecules will create fewer defects.

**(4) Tunable Properties.** Both the Inpria and Cornell approaches start by creating the $HfO_2$ nanoparticles followed by modification. These systems are relatively fixed in composition, and it may be quite difficult to overcome some of the limitations that currently face these resists. On the other hand, our molecular organometallic resists should be very tunable since our synthetic approach will enable excellent control over molecular structure, and therefore, excellent control over kinetic and thermodynamic properties.

## D. Initial Review of Periodic Table

We have calculated the EUV optical density of the elements from hydrogen (Z = 1) to Radium (Z = 88) using the standard-state densities (Table 1) and using Henke's filter transmission calculator.[9] We found that 38 elements have EUV ODs of > 11 /μm, but from among these we eliminated those elements that are exorbitantly expensive, radioactive, or toxic, leaving the 25 elements shown in red in Table 1.

We then reviewed the chemistry and reactivity of these 30 elements to find compounds which should:

- Produce films with high EUV OD
- Be stable to air and moisture
- Be soluble in organic solvents or water
- Have a good chance to be reactive to EUV photons and/or secondary electrons resulting in a change in solubility (either positive or negative tone).

This review of the chemistry of the remaining 88 elements resulted in five classes of compounds which we propose to investigate in this program:

- Mono-Nuclear Organometallic or Inorganic Compounds
- Transition Metal Oxide/Oxo-Carboxylate Clusters
- Tin Oxoclusters
- Bismuth-Cluster Chemistry
- Iron-Sulfide Clusters

## 2. Experimental Approach

Because the proposed research is so revolutionary, we will need to start this program by addressing much more fundamental questions about material properties than would typically be required resists based on organic polymers (e.g. coating, air stability). We will start by synthesizing new molecules at both SUNY New Paltz and CNSE. Simultaneously, we will purchase all the commercially available mononuclear compounds described in Section 3B. These commercially available compounds will "prime the pump" and allow us to quickly start evaluating the capabilities of EUV resists based on organometallic/inorganic compounds (Figure 3).

**Coating Quality.** We will start by dissolving the high OD compounds in organic solvents or water and spin coating to a target thickness of 20 nm. We will determine if they give high quality, uniform coatings using visual inspection and spectroscopic ellipsometry. If they are not amorphous (e.g. crystalline), we may re-design their structure (ligand exchange) or we may use additives to disrupt their tendency to crystallize. If their viscosity is insufficient to produce 20 nm films, we may need to add small quantities of high molecular weight polymers (e.g. polyvinylalcohol,[10] polyethyleneoxide, polymethylmethacrylate) to increase viscosity sufficiently to coat to 20 nm.

**Table 1. Optical and mass densities of the first 88 elements.** Elements marked with $$ have been rejected because they are too expensive; elements marked with RA have been rejected because they are radioactive; elements marked with Tox have been eliminated because they are too toxic.

| Z | Symbol | Density g/cm3 | EUV OD/um | Z | Symbol | Density g/cm3 | EUV OD/um | Note | Z | Symbol | Density g/cm3 | EUV OD/um | Note |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | H | 0.09 | 0.1 | 31 | Ga | 6.1 | 15.9 | | 61 | Pm | 7.3 | 5.5 | |
| 2 | He | 0.1785 | 0.6 | 32 | Ge | 5.35 | 13.1 | | 62 | Sm | 7.52 | 6.9 | |
| 3 | Li | 0.534 | 4.3 | 33 | As | 5.73 | 11.0 | | 63 | Eu | 5.24 | 5.0 | |
| 4 | Be | 1.85 | 0.7 | 34 | Se | 4.81 | 6.5 | | 64 | Gd | 7.9 | 6.8 | |
| 5 | B | 2.31 | 1.6 | 35 | Br | 3.12 | 2.4 | | 65 | Tb | 8.23 | 8.9 | |
| 6 | C | 2.25 | 2.8 | 36 | Kr | 3.74 | 7.7 | | 66 | Dy | 8.55 | 10.9 | |
| 7 | N | 1.25 | 2.8 | 37 | Rb | 1.63 | 0.3 | | 67 | Ho | 8.8 | 10.3 | |
| 8 | O | 1.43 | 4.9 | 38 | Sr | 2.54 | 0.5 | | 68 | Er | 9.07 | 10.9 | |
| 9 | F | 1.69 | 7.5 | 39 | Y | 4.47 | 0.9 | | 69 | Tm | 9.32 | 11.4 | |
| 10 | Ne | 0.9 | 5.3 | 40 | Zr | 6.51 | 1.5 | | 70 | Yb | 6.9 | 8.9 | |
| 11 | Na | 0.97 | 6.3 | 41 | Nb | 8.57 | 2.1 | | 71 | Lu | 9.84 | 10.9 | |
| 12 | Mg | 1.74 | 11.2 | 42 | Mo | 10.22 | 2.6 | | 72 | Hf | 13.31 | 14.0 | |
| 13 | Al | 2.7 | 12.0 | 43 | Tc | 11.5 | 4.9 | | 73 | Ta | 16.65 | 16.5 | |
| 14 | Si | 2.33 | 0.7 | 44 | Ru | 12.37 | 6.9 | | 74 | W | 19.35 | 13.4 | |
| 15 | P | 1.82 | 0.8 | 45 | Rh | 12.41 | 12.6 | $$ | 75 | Re | 21.04 | 16.1 | $$ |
| 16 | S | 2.07 | 1.4 | 46 | Pd | 12.02 | 18.8 | $$ | 76 | Os | 22.6 | 17.6 | $$ |
| 17 | Cl | 3.21 | 2.6 | 47 | Ag | 10.5 | 32.1 | | 77 | Ir | 22.4 | 17.9 | $$ |
| 18 | Ar | 1.78 | 1.6 | 48 | Cd | 8.65 | 22.2 | Tox | 78 | Pt | 21.45 | 24.3 | $$ |
| 19 | K | 0.86 | 0.9 | 49 | In | 7.31 | 28.3 | | 79 | Au | 19.32 | 20.9 | $$ |
| 20 | Ca | 1.54 | 1.4 | 50 | Sn | 7.31 | 29.4 | | 80 | Hg | 13.55 | 18.0 | Tox |
| 21 | Sc | 2.99 | 3.7 | 51 | Sb | 6.68 | 27.2 | | 81 | Tl | 11.85 | 17.0 | Tox |
| 22 | Ti | 4.5 | 7.0 | 52 | Te | 6.24 | 30.3 | | 82 | Pb | 11.35 | 19.9 | Tox |
| 23 | V | 5.96 | 9.8 | 53 | I | 4.93 | 23.6 | | 83 | Bi | 9.75 | 22.4 | |
| 24 | Cr | 7.2 | 15.6 | 54 | Xe | 5.9 | 29.8 | | 84 | Po | 9.3 | 22.5 | RA |
| 25 | Mn | 7.47 | 13.0 | 55 | Cs | 1.87 | 7.9 | | 85 | At | | | RA |
| 26 | Fe | 7.86 | 21.0 | 56 | Ba | 3.59 | 2.9 | | 86 | Rn | 9.73 | 29.7 | RA |
| 27 | Co | 8.92 | 26.7 | 57 | La | 6.15 | 2.0 | | 87 | Fr | | | RA |
| 28 | Ni | 8.9 | 29.2 | 58 | Ce | 6.77 | 2.5 | | 88 | Ra | 5.5 | 21.0 | RA |
| 29 | Cu | 8.94 | 24.7 | 59 | Pr | 6.77 | 3.0 | | | | | | |
| 30 | Zn | 7.14 | 22.4 | 60 | Nd | 7.01 | 5.2 | | | | | | |

**Solubility and Film Stability.** One our first tests of the new 20-nm films will be to determine their dissolution rates. Additionally, we will use this simple, inexpensive test to evaluate the air/moisture stability of these organometallic films.

**EUV Sensitivity.** The Berkeley Direct Contrast Tool (DCT) is an extremely convenient and effective tool for rapidly screening new resist formulations. It can expose ~6 wafers/hour and does not require outgassing tests prior to use.[11] We will screen resists for both positive and negative tone imaging using development times equal to 0.5X and 1.5X the clear time. We should get a wealth of information from these experiments.

The initial screening of commercially availability compounds will be helpful in determining the EUV photoreactivity of certain structural features such as metal identity, cluster type, and ligand type. These relatively simple early tests will help guide the design and synthesis of more complex cluster compounds.

**Outgassing Tests and Lithographic Evaluation.** Once we have identified the EUV sensitivity of our organometallic films, we will test them for mass-spectral outgassing using the CNSE RoX tool. Once the films pass this test, we will image them on the BMET and AMET. Most likely, initial imaging experiments will be performed on the Berkeley tool since this facility is much more flexible with regard to process and development than is the AMET facility.
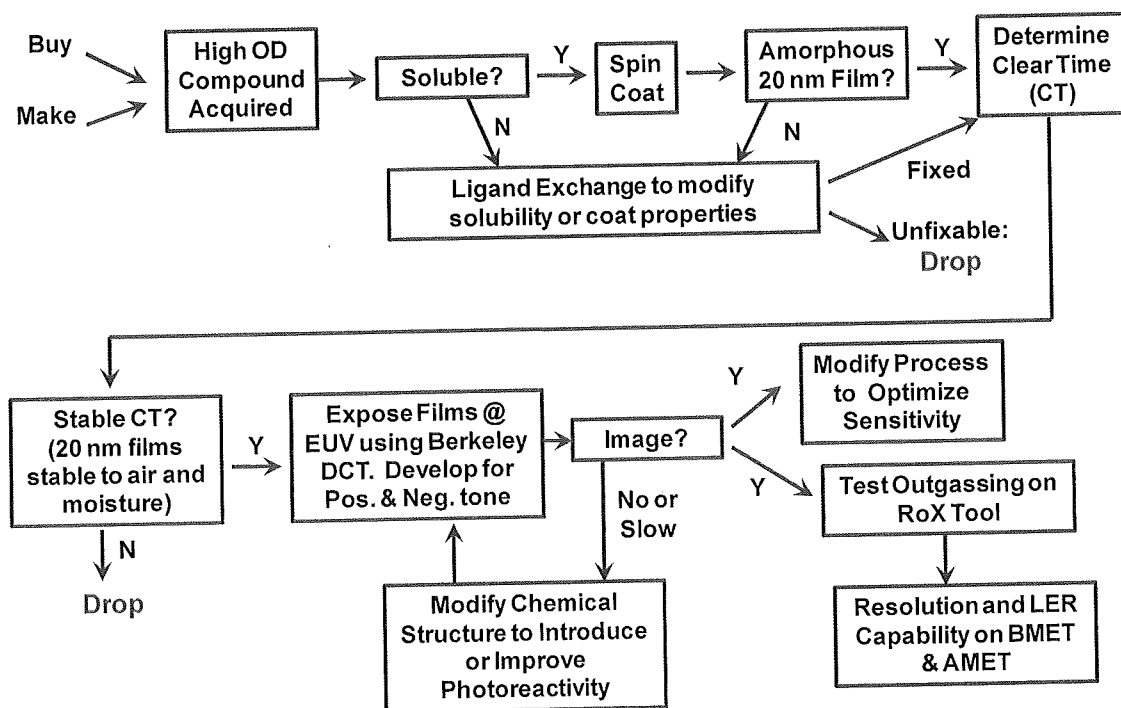
**Figure 3.** Flow chart for evaluating new organometallic compounds for use in EUV Lithography.

## 3. Five Material Classes to be Investigated

Our analysis of the inorganic and organometallic literature has resulted in the identification of five classes of compounds which we propose have the best chance of providing high-resolution materials for EUV Lithography. This section starts with a brief discussion of the kinds of photochemical reactions that are possible upon exposure to EUV light (and secondary electrons), then follows with a detailed discussion of each class of materials.

### A. Possible Photochemistry of High-OD Organometallic Films.

Since the photochemistry of transition and main group metal complexes has never been studied at EUV, we can only speculate on the types of reactions that will be observed. Further, it might be best to avoid organometallic compounds which exhibit photochemical reactivity at longer wavelengths since these compounds might have significant sensitivity to Out of Band (OoB) radiation, with very little sensitivity to EUV light. Fortunately, the EUV photolysis of $HfO_2$ gives some useful hints. Outgassing tests have shown that molecular oxygen is produced during the EUV photolysis of $HfO_2$, indicating that the oxide ions are being oxidized and must be accompanied by the reduction of Hf(IV).[8] If this reaction is common with other metal-ligand systems, *it strongly suggests we can synthesize metal complexes that will be much more reactive toward EUV radiation,* since Hf(IV) is very difficult to reduce (Figure 4). Note that Hf(IV) is more than 1.5 volts harder to reduce than Sn(IV), W(VI), or Bi(III) in reasonably comparable conditions. In fact, almost any metal ion would be easier to reduce than Hf(IV). One useful strategy would be to prepare a variety of metal-oxo clusters of these or similar metals. EUV photolysis should generate $O_2$ with a concomitant reduction of the metal ions.

$$HfO(OH)_{2(s)} + H_2O_{(l)} + 4e^- \longrightarrow Hf_{(s)} + 4OH^-_{(aq)} \qquad E^o = -2.50 \text{ V}$$

$$WO_4{}^{2-}{}_{(aq)} + 4H_2O_{(l)} + 6e^- \longrightarrow W_{(s)} + 8OH^-_{(aq)} \qquad E^o = -1.06 \text{ V}$$

$$SnO_{2(s)} + 2H_2O_{(l)} + 4e^- \longrightarrow Sn_{(s)} + 4OH^-_{(aq)} \qquad E^o = -0.945 \text{ V}$$

$$Bi_2O_{3(s)} + 3H_2O_{(l)} + 6e^- \longrightarrow 2Bi_{(s)} + 6OH^-_{(aq)} \qquad E^o = -0.46 \text{ V}$$
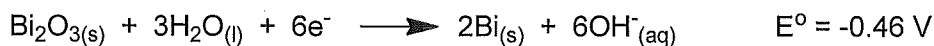
**Figure 4.** Comparison of relevant reduction potentials.

Given the ability to design molecular complexes, we can also make the photochemistry more facile by replacing the oxide ion with ligands that are more easily oxidized. If EUV photolysis can result in the oxidation of oxide, any organic ligand will also be oxidized under these conditions. We will focus on simple ligands with C-O bonds because they are readily available and they may outgas the fairly benign molecule of $CO_2$ rather than more corrosive gases. A range of possible ligands is shown in Figure 5. A significant advantage in using molecular complexes is that the reactivity of the ligands can be readily "tuned" by varying the structure and substituents. For instance, oxalate complexes are expected to be quite reactive because oxalate is readily oxidized by two electrons to give two equivalent of $CO_2$, while the carboxylate and β-diketonate ligands will be less reactive.
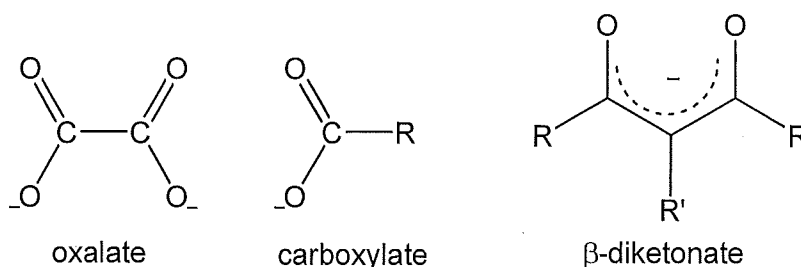


**Figure 5.** Several ligands that can be used to induce photochemical responses at EUV.

Two possible photochemical mechanisms are shown in Figure 6, both of which could reasonably result in a significant change in solubility properties. In Mechanism 1, a metal oxide cluster releases $O_2$ with the reduction of the metal which would likely result in a chance in solubility vs. the starting material. In Mechanism 2, an oxalate complex reacts with the loss of $CO_2$, leaving two open coordination sites. Formation of a dimer by reaction with another complex or further reaction to give larger oligomers (not shown) should significantly change solubility.
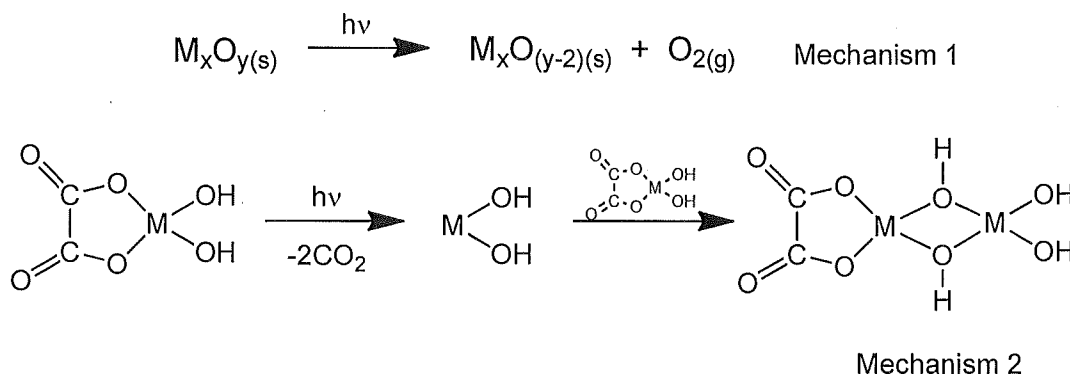


$$M_xO_{y(s)} \xrightarrow{\ h\nu\ } M_xO_{(y-2)(s)} + O_{2(g)} \qquad \text{Mechanism 1}$$

Mechanism 2

**Figure 6.** Possible photochemical mechanism for metal complexes.

The compounds that we propose to study have either a single metal ion or up to twelve metals ions with the counter ion/ligands being either $O^{2-}$ or oxygen-containing organic ligands. In all of these compounds, either or both of these mechanisms could be observed. Most of the compounds proposed are prototypical examples of an enormous number of derivatives that can be used to optimize their physical or chemical properties.

## B. Mono-Nuclear Organometallic or Inorganic Compounds

The first compounds to be evaluated will be mono-nuclear, since they are typically commercially available or easily prepared. These compounds are excellent candidates be begin our testing, since they are widely available with different metals and with different ligands, such as acetylacetate (acac), $F_3$-acac, $F_6$-acac, acetate and oxylate (Figure 7). These compounds can span a large area of different chemistries, lending insight into the EUV photochemistry of these ligands and metals. Ultimately, we think that cluster compounds will make the best resists, however, these early studies with mono-nuclear compounds will help direct the selection of which cluster compounds to synthesize.

**Calculations of Mass-Density and EUV Transmittance in 20 nm Films.** To allow us to compare target molecules, we have calculated the mass-density ($\rho$) and EUV transmittance of target molecules shown below and throughout the remainder of this proposal. Since the density of most organometallic compounds is unknown, densities were calculated through a weighted average of each element and its standard state.[9] Transmittance (T) values were calculated using Henke's filter transmission at 13.5 nm wavelength for a 20 nm film. As mentioned in Section 1, the target transmittance is T = 0.5.

Mn(acac)$_2$
B1: $\rho = 3.1$ g/cm$^3$
T = 0.76

Mn(acac)$_3$
B2: $\rho = 2.7$ g/cm$^3$
T = 0.79

Cu(acetate)
B3: $\rho = 5.5$ g/cm$^3$
T = 0.52

Sn(acetate)$_2$
B4: $\rho = 4.5$ g/cm$^3$
T = 0.51

Co(acac)$_2$
B5: $\rho = 3.5$ g/cm$^3$
T = 0.70

Co(acac)$_3$
B6: $\rho = 3.0$ g/cm$^3$
T = 0.75

Ag(acetate)
B7: $\rho = 7.4$ g/cm$^3$
T = 0.38

SnI$_2$
B8: $\rho = 5.7$ g/cm$^3$
T = 0.30

Fe(acac)$_3$
B9: $\rho = 2.8$ g/cm$^3$
T = 0.77

Al(acac)$_3$
B10: $\rho = 1.9$ g/cm$^3$
T = 0.83

Ni(acetate)$_2$
B11: $\rho = 4.1$ g/cm$^3$
T = 0.60

SnI$_4$
B12: $\rho = 5.4$ g/cm$^3$
T = 0.32

Ni(acac)$_2$
B13: $\rho = 3.4$ g/cm$^3$
T = 0.70

Ni(F$_3$-acac)$_2$
B14: $\rho = 3.0$ g/cm$^3$
T = 0.66

Zn(acac)$_2$
B15: $\rho = 3.1$ g/cm$^3$
T = 0.73

Zn(F$_6$-acac)$_2$
B16: $\rho = 2.5$ g/cm$^3$
T = 0.68

Na[M(2,2'-bpy)(C$_2$O$_4$)$_2$]
M = Cr, Fe, Co
B17: $\rho =$   2.4   2.6   2.8 g/cm$^3$
T = 0.77  0.74  0.72

Na$_3$[M(C$_2$O$_4$)$_3$]
M = Cr, Fe, Co
B18: $\rho =$   2.3   2.4   2.6 g/cm$^3$
T = 0.70  0.68  0.66

[M(2,2'-bpy)$_2$(C$_2$O$_4$)]Cl
M = Cr, Fe, Co
B19: $\rho =$   2.0   2.7   2.8 g/cm$^3$
T = 0.85  0.80  0.79

[M((2,2'-bpy)$_3$]Cl$_3$
M = Cr, Fe, Co
B20: $\rho =$   2.6   2.7   2.8 g/cm$^3$
T = 0.85  0.84  0.83

**Figure 7.** Some commercially available acetates and acetylacetates (acac). Mass-density ($\rho$) and EUV transmittance (T) are shown for each target molecule.

## C. Transition Metal Oxide/Oxo-Carboxylate Clusters

We propose to examine two types of transition-metal oxide clusters: polyoxometallates (POM) compounds and oxo-carboxylates. Polyoxometallates are metal-oxo anionic clusters formed by early transition metals.[12] The number of metal ions can range from as few as six to greater than fourty. We will focus on tungsten-containing POMs because of their high density. A number of these compounds have simple, well-tested syntheses (Figure 8).[13]

$H_3[P(W_{12}O_{40})]$

C1: $\rho = 15.2$ g/cm$^3$
T = 0.40

$Na_3[PW_{12}O_{40}]$

C2: $\rho = 14.8$ g/cm$^3$
T = 0.40

$Cs_6[P_2W_5O_{23}]$

C3: $\rho = 9.3$ g/cm$^3$
T = 0.35

$Na_9[SiW_{11}O_{39}]$

C4: $\rho = 14.0$ g/cm$^3$
T = 0.33

$[NBu_4]_2[W_{10}O_{33}]$

C5: $\rho = 13.1$ g/cm$^3$
T = 0.46

$[NBu_4]_2[W_6O_{19}]$

C6: $\rho = 12.0$ g/cm$^3$
T = 0.50

$Na_8[SiW_{11}O_{39}]$

C7: $\rho = 14.1$ g/cm$^3$
T = 0.34

**Figure 8.** Polyoxometalate compounds. Mass-density ($\rho$) and EUV transmittance (T) are shown for each target molecule.

Carboxylate-bridged, transition metal clusters are also another very large group of complexes. Many transition metals will form dimer, trimers, and tetramers with the metals bridged by carboxylate and oxide ligands. Although these are similar to the POMs in some ways, the presence of the carboxylate ligand provides for greater variation in the chemistry of the complexes because of the R group on the carboxylate. Several examples with known synthetic pathways are shown in Figure 9.[14-16]
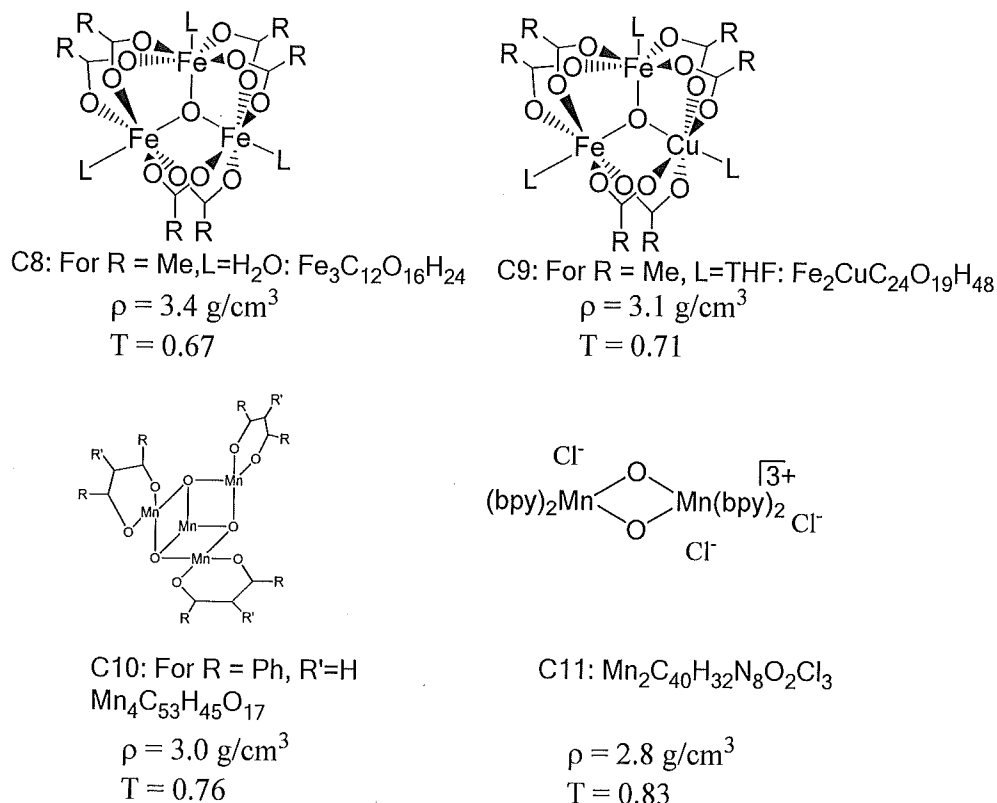
C8: For R = Me, L = $H_2O$: $Fe_3C_{12}O_{16}H_{24}$
$\rho = 3.4$ g/cm$^3$
T = 0.67

C9: For R = Me, L = THF: $Fe_2CuC_{24}O_{19}H_{48}$
$\rho = 3.1$ g/cm$^3$
T = 0.71

C10: For R = Ph, R'=H
$Mn_4C_{53}H_{45}O_{17}$
$\rho = 3.0$ g/cm$^3$
T = 0.76

C11: $Mn_2C_{40}H_{32}N_8O_2Cl_3$
$\rho = 2.8$ g/cm$^3$
T = 0.83

**Figure 9.** Oxo-carboxylate compounds. Mass-density ($\rho$) and EUV transmittance (T) are shown for each target molecule.

## D. Tin Oxoclusters.

The chemistry of tin is very rich. It forms anionic clusters containing only tin,[17-19] forms polymers,[20-22] and forms oxoclusters.[23-26] Tin oxoclusters are three-dimensional inorganic molecules containing Sn-O bonds. The most published tin oxocluster has the formula $(RSn)_{12}O_{14}(OH)_6L_4$, where R is generally aliphatic and L is a ligand. This class of compounds has been established as relatively stable clusters, with a large amount of tin and oxygen giving it the potential to be highly EUV absorbing. These compounds can be made fairly easily through dehydration of $RSn(OH)O$[25-26] or by hydrolysis of the trihalide $RSnCl_3$[23-24] in the presence of a ligand (L). Furthermore, tin has the advantage of NMR accessibility, having both $^{117}Sn$ and $^{119}Sn$ isotopes with spin ½ nuclei.

Tin oxoclusters are known to be very stable in solution, stable to oxygen and water, and generally very thermally stable (up to ~250 °C).[25-26] This stability has some dependence on the associated ligand (L). The oxocluster D1 is stable in solution and forms stable crystals which are soluble in benzene and chloroform (Figure 10). Since tin has a relatively low redox potential (($Sn^{4+} + 2e^- \rightarrow Sn^{2+}$) $E^{\circ}_{red} = 0.15V$), it should have significantly greater sensitivity towards undergoing ligand oxidation than a comparable hafnium oxide compound.
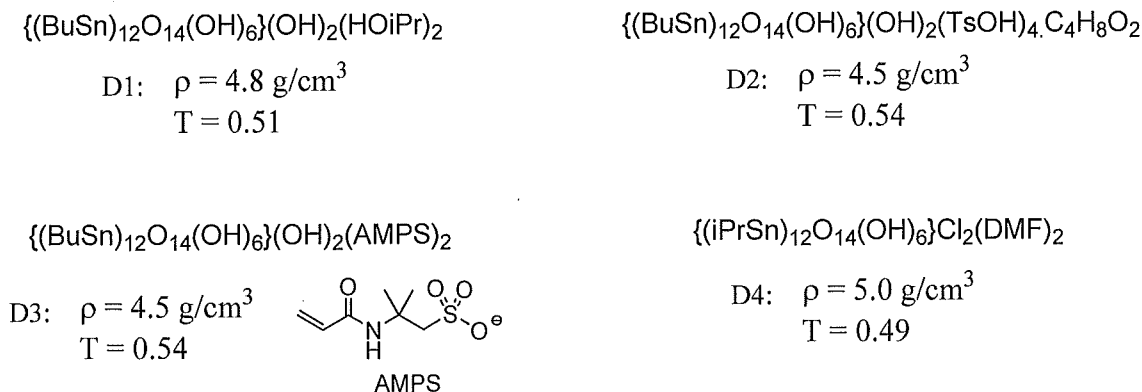
{(BuSn)$_{12}$O$_{14}$(OH)$_6$}(OH)$_2$(HOiPr)$_2$

D1:  $\rho = 4.8$ g/cm$^3$

T = 0.51

{(BuSn)$_{12}$O$_{14}$(OH)$_6$}(OH)$_2$(TsOH)$_4$.C$_4$H$_8$O$_2$

D2:  $\rho = 4.5$ g/cm$^3$

T = 0.54

{(BuSn)$_{12}$O$_{14}$(OH)$_6$}(OH)$_2$(AMPS)$_2$

D3:  $\rho = 4.5$ g/cm$^3$

T = 0.54

AMPS

{(iPrSn)$_{12}$O$_{14}$(OH)$_6$}Cl$_2$(DMF)$_2$

D4:  $\rho = 5.0$ g/cm$^3$

T = 0.49

**Figure 10.** Tin oxoclusters. Mass-density ($\rho$) and EUV transmittance (T) are shown for each target molecule.

## E. Bismuth-Clusters

Bismuth is the largest atom in the periodic table that is not radioactive. It is also one of the few heavy metals that is non-toxic (an ingredient in peptobismal). It is very dense, has a high absorbance in EUV, and forms very stable oxides. Bismuth comes in many forms,[27] the most stable being oxoclusters such as Bi$_6$O$_4$(OH)$_4$L$_n$, where n ranges from 3 to 6 (Figure 11).[28-32] These bismuth oxoclusters are very stable (in solution and solid state), and are frequently used as catalysts in high-temperature organic reactions.[28] The oxoclusters are generally made by thermal decomposition of Bi$_2$O$_3$ in water[28] or BiPh$_3$ in toluene[29] in the presence of a ligand (L).

[Bi$_9$O$_8$(OH)$_6$][CF$_3$SO$_3$]$_5$

E1:  $\rho = 7.0$ g/cm$^3$

T = 0.43

Bi$_9$O$_7$(OCH(CF$_3$)$_2$)$_{13}$

E2:  $\rho = 4.5$ g/cm$^3$

T = 0.47

[Bi$_6$O$_4$(OH)$_4$(H$_2$O)$_2$][(CH$_2$)$_2$(SO$_3$)$_2$]$_3$
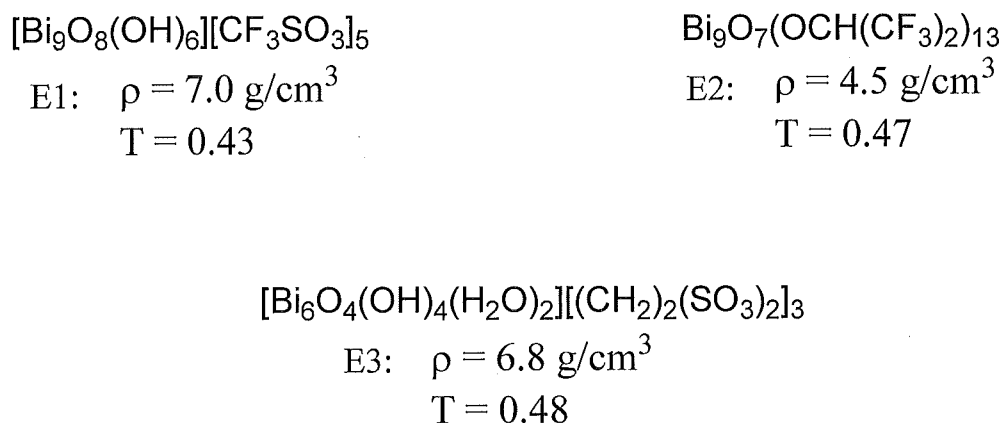
E3:  $\rho = 6.8$ g/cm$^3$

T = 0.48

**Figure 11.** Bismuth oxoclusters. Mass-density ($\rho$) and EUV transmittance (T) are shown for each target molecule.

## F. Iron-Sulfide Clusters

Iron-sulfide clusters represent a large class of compounds that are relatively easy to prepare,[33-35] some of which are stable under atmospheric conditions. The core structure is a cube formed by four iron atoms (either +2 or +3) and four, triply-bridging ligands (Figure 12) which are usually sulfide ions. The iron atoms are ligated by a mono-dentate anionic ligand that can vary widely.

Although much isn't known about their photochemistry, it seems likely that under the punishing conditions of EUV photolysis, ligands would be expelled (with or without redox changes) leading to open coordination sites on one or more of the irons. A desirable scenario would be for the iron-sulfide cubes to remain after development, leaving highly insoluble materials such as FeS or Fe$_2$S$_3$ (Figure 13).

There are many possible iron-sulfide candidates to test, but it is important for the compounds to be stable under atmospheric conditions and relatively easy to synthesize. One likely candidate is $Fe_4S_4(NO)_4$. In addition to the compound being stable and simple to prepare, it has the added attractive feature that NO is a ligand that is known to be expelled photochemically. We do not expect that NO or its oxidative byproducts would be difficult to remove from the surface of EUV optics.
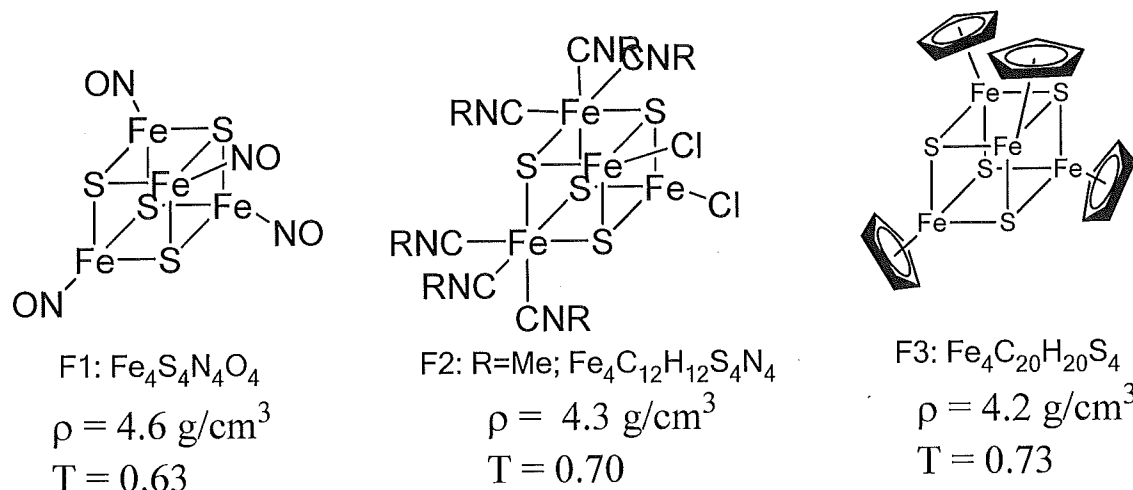


F1: $Fe_4S_4N_4O_4$
$\rho = 4.6 \text{ g/cm}^3$
$T = 0.63$

F2: R=Me; $Fe_4C_{12}H_{12}S_4N_4$
$\rho = 4.3 \text{ g/cm}^3$
$T = 0.70$

F3: $Fe_4C_{20}H_{20}S_4$
$\rho = 4.2 \text{ g/cm}^3$
$T = 0.73$

**Figure 12.** Iron sulfide clusters. Mass-density ($\rho$) and EUV transmittance (T) are shown for each target molecule.



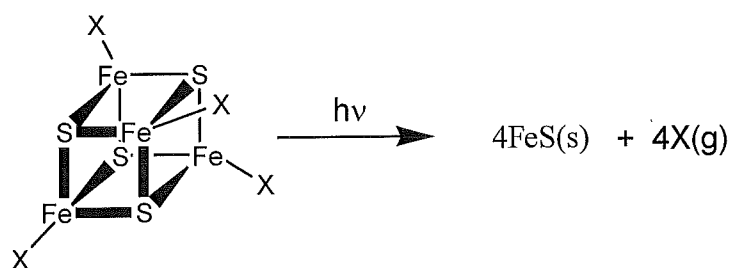$$4FeS(s) \; + \; 4X(g)$$

**Figure 13.** Possible photochemistry of metal-sulfide clusters.

### 4.  Target Deliverables

**Year 1.**
- **Purchase 12-18 mononuclear compounds and raw materials for other synthetic targets.**
- **Synthesize 2-6 mononuclear compounds.**
- **Conduct Compound/Resist Evaluation Cycles:**
  - New materials will be evaluated for: coating quality, film stability (air, humidity), EUV sensitivity (open frame on LBNL DCT).
  - Samples that do not pass initial evaluations will be either rejected, or redesigned, re-synthesized, and reevaluated until they pass.
  - Resists that show EUV sensitivity will be tested for MS outgassing.
  - Resists that show EUV sensitivity and pass outgassing will be imaged on the BMET for EUV resolution, LWR, and sensitivity.

*Page 15 of 18*

- **Synthesize 8-12 cluster compounds**
- **Conduct Compound/Resist Evaluation Cycles:**
  - New materials will be evaluated for: coating quality, film stability (air, humidity), EUV sensitivity (open frame on LBNL DCT).
  - Samples that do not pass initial evaluations will be either rejected, or redesigned, re-synthesized, and reevaluated until they pass.
  - Resists that show EUV sensitivity will be tested for MS outgassing.
  - Resists that show EUV sensitivity and pass outgassing will be imaged on the BMET for EUV resolution, LWR, and sensitivity.

**Ultimately, we propose to identify 3-5 new material "platforms" from which to build new resist technologies.**

**Year 2.**
- Optimize the lithographic properties of these 3-5 new material platforms through synthesis and testing of physical and lithographic properties.
- Synthesis/Formulation/Lithographic cycles of learning through Conduct Compound/Resist Evaluation Cycles:
  - New materials will be evaluated for: coating quality, film stability (air, humidity), EUV sensitivity (open frame on LBNL DCT).
  - Samples that do not pass initial evaluations will be either rejected, or redesigned, re-synthesized, and reevaluated until they pass.
  - Resists that show EUV sensitivity will be tested for MS outgassing.
  - Resists that show EUV sensitivity and pass outgassing will be imaged on the BMET for EUV resolution, LWR, and sensitivity.
- Explore mechanistic insight into photochemical reaction mechanisms
- Determine bulk etch resistance of new material sets using oxide and fluorocarbon etch chemistries.
- Direct measurements of EUV OD of resist films (either reflection studies on multilayers or mass-density studies by $XR^2$).
- Conduct Out of Band (OoB) sensitivity studies of most promising candidates.

**Year 3.**
- Through a series of cycles of synthesis, formulation, lithography we will optimize the process and composition of molecular organometallic resists completing resist goals:
  - Improvements in resolution, LWR and sensitivity
  - 10 nm half-pitch resolution
  - < 1 nm LWR
- Conduct and pass witness plate outgassing tests.
- With help from Intel, we will perform metallic contamination studies of new resists (negotiable).
- Provide samples to resist or material vendors to determine interest in commercializing technology.

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